Assessing Potentially Important Factors Contributing to Ozone

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Introduction

- The photochemical interaction of VOC and NO_x form ozone.
- Each VOC reacts at a different rate and with different reaction mechanisms.
- EPA's VOC control strategy for nonattainment areas is to reduce the emissions of all VOCs without regard to an individual compound's chemical ability to form ozone.
- The chemical ability of an individual compound to form ozone is considered in the definition of VOC (40 CFR 51.100). Compounds EPA determines to be less reactive than ethane on a molar basis may be classified as "negligibly reactive" and excluded from the definition of VOC for State Implementation Plans.

Ozone Formation

- Ozone is a secondary pollutant formed by the reaction of nitrogen oxides and hydrocarbons. Motor vehicle exhaust, industrial emissions, gasoline vapors, biogenic hydrocarbon emissions, and chemical solvents are some of the major sources of NO_x and hydrocarbons, also known as ozone precursors. These precursors have both anthropogenic and biogenic origins. The formation of ozone begins with the photodissociation of nitrogen dioxide (NO_2) in the presence of sunlight.

  NO_2 + sunlight = NO + O

- The atomic oxygen (O) quickly combines with molecular oxygen (O_2) to form ozone (O_3):

  $O + O_2 = O_3$

- Once formed, ozone reacts with NO to regenerate NO_2:

  $NO + O_3 = NO_2 + O_2$

- Most of the nitrogen oxides emitted into the atmosphere are emitted as NO; if ozone exists near where the NO is emitted, then the NO will reduce ozone concentrations by scavenging.

- However, VOCs remove the NO as shown (greatly simplified) next. Thus, NO is not available to re-combine with ozone to form NO_2 and therefore, ozone can accumulate.

  VOC + NO = NO_2 + other products

- The formation and accumulation of ozone may occur over a period of a few hours or over several days, depending on meteorological and other environmental conditions.

Ozone Critical Source Assessment Techniques

- **Relative age of hydrocarbon mixture**: analyses include assessing the spatial and temporal characteristics of ratios of selected species. These analyses are useful for assessing the potential significance of transport versus local generation of ozone.
- **Biogenic contribution to NMHC**: analyses include assessing the spatial and temporal characteristics of isoprene concentrations and weight fractions. These analyses are useful for understanding the importance of biogenic emissions relative to anthropogenic emissions.

Relative Age of Hydrocarbon Mixture

- Ratios of hydrocarbons may be used as tracers of urban emissions.
- The relative abundance of more-reactive species (olefins, xylenes) should decrease with time during the day, while less-reactive species (paraffins, benzene) will appear to increase.
- Comparisons of the ratios among sites can be made to estimate the relative age of air parcels and help provide evidence of transport. This analysis may also present evidence of the presence of fresh emissions or the presence of unique regional sources for a species.
- In this type of analysis, it is important to assess several different species ratios and look for consensus among the results.

Example Source Ratios from Tunnel Studies

Location	Ratio	1994	1995	1996	1997
Los Angeles (O'Connor et al., 1998)	benzene/acetylene toluene/benzene m-&p-xylenes/benzene propene/ethene		0.80 2.10 2.20 0.46	0.53 2.50 2.30 0.50	
San Francisco Bay Area (Kirchstetter et al., 1999)	benzene/acetylene toluene/benzene m-&p-xylenes/benzene propene/ethene	2.00 1.60 1.50 0.45	1.70 1.60 1.40 0.55	1.10 2.60 2.00 0.59	1.60 2.30 1.80 0.51
Vancouver, B.C. (Rogak et al., 1998)	benzene/acetylene toluene/benzene m-&p-xylenes/benzene propene/ethene		1.30 1.90 1.40 0.56		
New York, N.Y. (Gertler et al., 1996)	toluene/benzene m-&p-xylenes/benzene		2.50 1.40		

- In an analysis of age of an air mass, it is important to use ratios that are appropriate for the region and year of study.
- Note, in this example, that ratios varied widely among sites and years. These differences may reflect variations among source types, fuels, vehicle fleets, emission controls, etc.

Ambient Ratio Analysis

Median 0500-0800 PST ambient ratios at Southern California PAMS and PAMS-like sites in 1997.

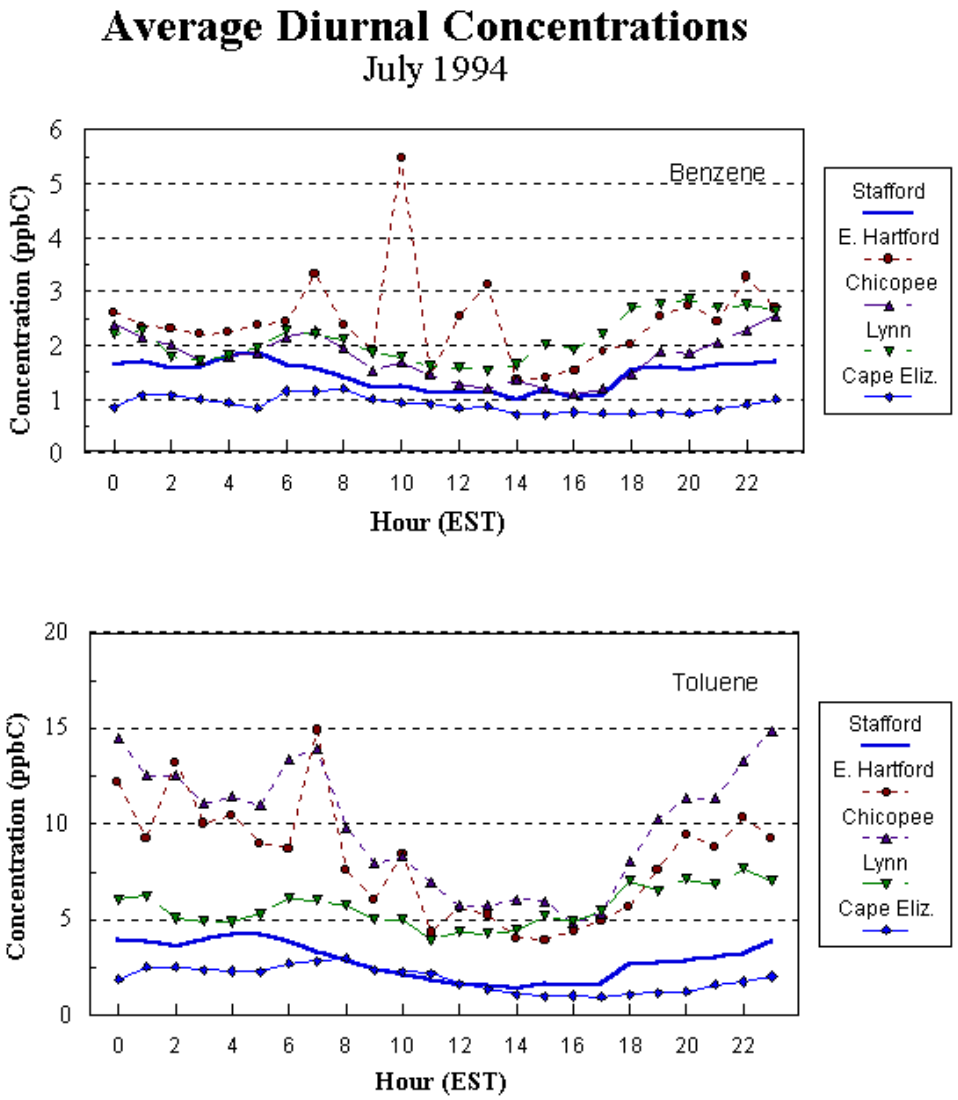
Location	Site Type	toluene/benzene	xylenes/benzenes	Assessment
Hawthorne	1	3.2	2.7	"Aged"
Burbank	1/2	4.0	3.3	"Fresh"
Los Angeles	Urban	3.6	3.0	"Fresh"
Pico Rivera	2	3.8	2.9	"Fresh"
Azusa	3	4.3	2.9	"Fresh"
Upland	4/1	3.6	2.8	"Mixed"
Banning	Downwind	2.9	1.6	"Aged"

In this example, ambient data from the upwind Hawthorne and downwind Banning sites appear to be more “aged” than the data from downtown Los Angeles. The results of the ratio analysis with these two ratios at Upland are mixed: the toluene/benzene ratio similar to Los Angeles, but the xylenes/benzene ration indicating aging.

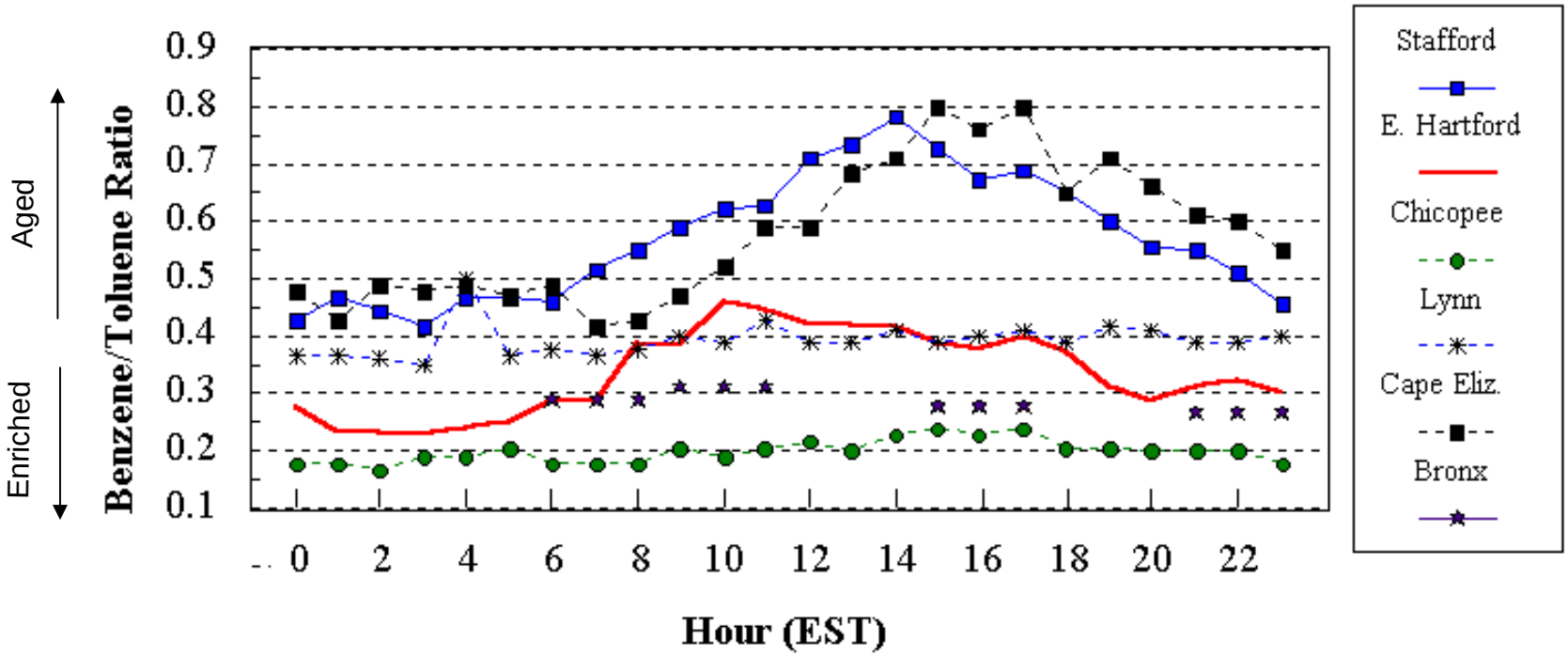
Main et al., 1999

Assessing Relative Age (1 of 3)

- Before investigating diurnal ratios, inspect the diurnal behavior of individual VOCs in the ratio. In the example shown, toluene concentrations are generally lower at the downwind sites of Stafford and Cape Elizabeth that at the urban sites.
- Comparison of the diurnal variation in a hydrocarbon at multiple sites can show the existence of different sources. For example, note the higher daytime benzene concentrations at the East Hartford site.
- Scatter plots and relationships of concentration and wind direction are also useful to investigate.



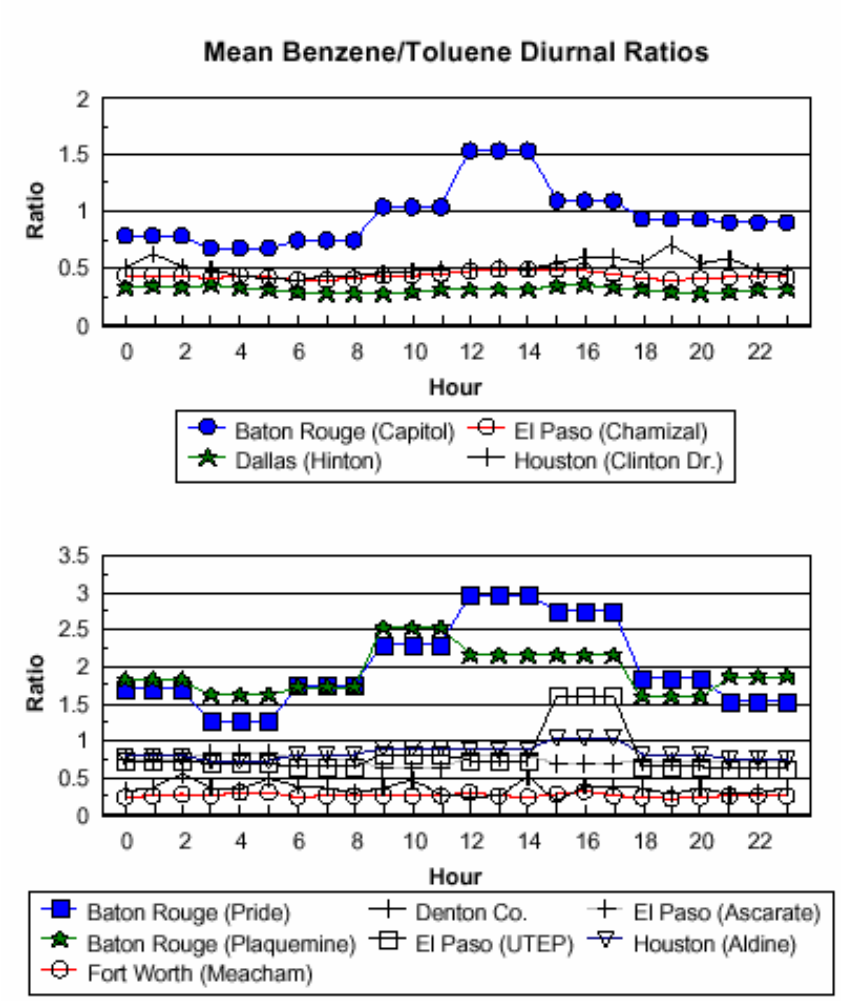
Assessing Relative Age (2 of 3)



- In this example, the ratio was highest at the downwind sites of Stafford and Cape Elizabeth during the day indicating the most aged air; this is consistent with the location of these sites with respect to urban centers.
- B/T ratios at Lynn change little with time of day indicating fresh emissions. Ratios at East Hartford are similar to Lynn during the day, but decrease at night (possible nighttime toluene source?). Chicopee shows possible toluene sources (enrichment).

Assessing Relative Age (3 of 3)

- In this example, the top figure shows the mean benzene to toluene ratios measured at the Baton Rouge Capitol site compared to ratios from urban sites in Texas. The bottom figure compares mean ratios at other Baton Rouge and Texas sites.
- All the Baton Rouge sites have higher benzene/toluene ratios (possibly indicating more aged air) than the sites analyzed in Houston, Dallas, and El Paso. The more downwind sites of Pride and Plaquemine near Baton Rouge are more influenced by aged air masses than the Capitol site.



Sather and Kemp, 1998

Estimating Air Parcel Age (1 of 2)

- Estimating air parcel age assumes the following:
  - Atmospheric removal of hydrocarbons occurs primarily through gas-phase reaction with the OH radical (e.g., $k_X = 1.9 \times 10^{-11}$ and $k_B = 1.18 \times 10^{-12} cm^3$ molecule$^{-1}s^{-1}$).
  - Average source ratios can be established and are applicable to your region (e.g., $X/B_{source} = 1.5$).
  - Dilution by air masses of different ages is negligible.
  - The OH radical mixing ratio is known (e.g., 1.5×10^6).
- Gong and Demerjian's (1997) equation:

$$\ln \frac{(X/B)_{amb.}}{(X/B)_{source}} = -(k_X - k_B)[OH]t$$

Where X = m-&p-xylenes
B = benzene
$(X/B)_{amb.}$ = 0.7
t = 8.7 hours

Estimating Air Parcel Age (2 of 2)

- The sites located nearest fresh motor vehicle emissions exhibited the lowest air parcel age (e.g., Duke, St. Augustine, Hattie Ave., and Charlotte Plaza). Estimated ages less than zero indicate that the ambient X/B ratio was higher than the assumed source X/B ratio.
- The afternoon samples showed aging compared to the morning samples (e.g., Butner, County Line in 1997).
- Some sites with morning samples showed evidence of aging in 1996 and 1997 (e.g., Pittsboro and York County) possibly indicating the presence of carryover/transport.

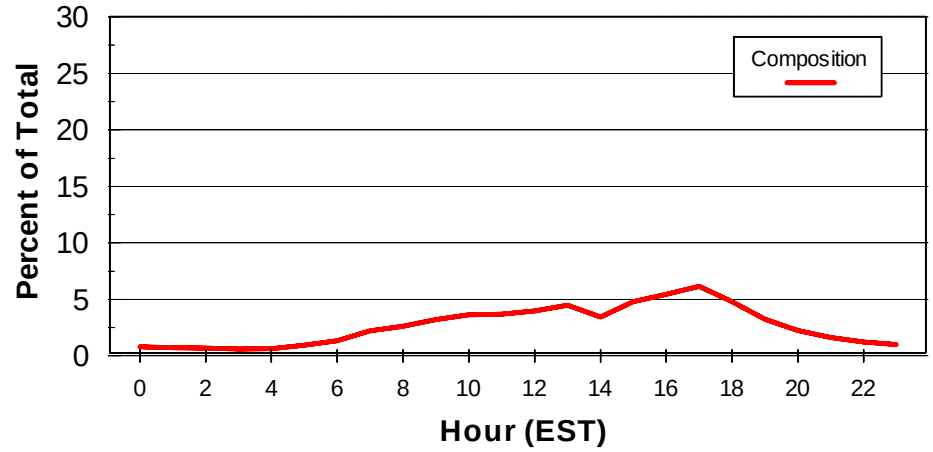
Site	Est. Time (hours) 1996	1997
Butner	***5.2***	***26*** [a]
County Line	3.9	***12*** [a]
Duke	0.4	1.1
St. Augustine	1.2	0.2
Enochville	***5.9***	***6.2*** [a]
Hattie Ave.	<0	<0
Pittsboro	***5.9***	***7.5***
Fuquay-Varina	4.0	3.2
Union Cross	3.5	<0
York County	5.0	***6.0***
Charlotte Plaza	0.5	<0

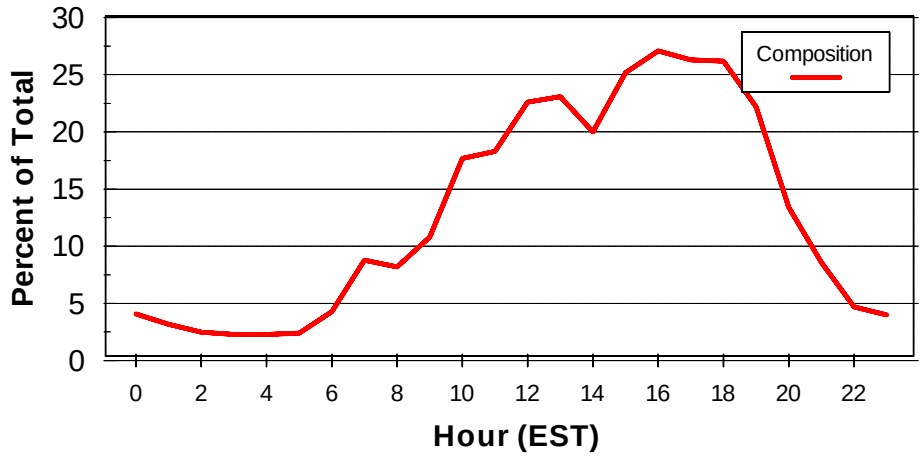
[a] afternoon samples
Bold/italic entries indicate estimated aging greater than 5 hours.

Estimated median air parcel age based on m-&p-xylenes to benzene ratios in 1996 and 1997 at several North Carolina sites. All samples were collected in the morning unless otherwise specified. (MacDonald et al., 1998)

Biogenic Contribution to Ambient NMHC

- Biogenic emissions, including isoprene, can be important to ozone formation even at some urban sites.
- In this example, isoprene typically accounts for less than 5% of the composition at urban East Hartford, CT.
- In contrast at rural Stafford, CT isoprene accounts for nearly 30% of the composition.





Average diurnal plot of the contribution of isoprene to total identified NMHC for July 1994.

Summary

- In this section, examples of several analyses were provided to illustrate how an analyst can explore ozone formation, the relative age of hydrocarbon mixtures, and the biogenic contribution to NMHC.
- No single analysis should form the basis for decisions on control strategies; rather, several analyses should be performed to form a consensus.

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